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CHARACTERIZATION OF ELECTROLESS NICKEL BY ESCA

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ABSTRACT

Electroless nickel (EN) deposits obtained from alkaline EN baths employing citrate or glycine as complexing agents and triethanolamine as an additive are characterized by ESCA. This study reveals that Ni and P in EN are present as $Ni^{\delta+}$ and $P^{\delta-}$ species. Besides these, NiO and $NiPO_4$ are present as surface species. They confer passivity on EN and thereby contribute to its corrosion resistance.

INTRODUCTION

Electroless nickel deposits obtained by using sodium hypophosphite as the reducing agent are binary alloys of nickel and phosphorus. In the as-plated condition, the deposits with low phosphorus content are crystalline and those containing more than 7 wt % of phosphorus are amorphous or microcrystalline. These deposits are reported to be in the metastable state. On heat treatment, they transform into a more stable state consisting of fcc Ni and tetragonal Ni_3P. Numerous efforts have been made to study the amorphous-crystalline transition by Transmission

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Electron Microscopy (TEM) and Differential Scanning Calorimetry (DSC) [1-17]. Sugila and Yeno [18] have studied by XPS EN deposited from a pyrophosphate bath. They have found that deposits obtained at pH = 9 contain mostly non-metallic nickel and considerable oxygen impurity throughout the deposit, and EN obtained at pH=10 **contains metallic nickel**. Papini and Papini [19] found that the deposit contained, besides Ni^o and P, oxidized nickel which was probably NiO and Ni_2O_3 or $Ni(OH)_2$. Ivanov *et al* [20] found that the surface layers contained Ni^o and NiO while deeper layers were free from NiO. P was seen to be present as $P^o$and P^{5+} throughout the bulk of the deposit. Significant amounts of NiO were reported to be present throughout the deposit in EN formed from pyrophosphate baths [21]. The purpose of this communication is therefore to get a better insight into the state of combination of P in EN and to elucidate the nature of surface species by photoelectron spectroscopic studies.

EXPERIMENTAL

Film preparation

Citrate or glycine based baths containing ethanolamine developed by two of the authors [22,23] were used to prepare **electroless** nickel films for XPS investigations. The bath composition and operating conditions are given in Tables I and II. Deposits with different phosphorus contents were prepared **from a** citrate-triethanolamine bath by varying the concentration of sodium citrate. Deposits from citrate-triethanolamine baths were designated as CT-EN and those from glycine-ethanolamine were designated as GM-EN, GD-EN and GT-EN where M,D,T stand for mono, di and tri ethanolamine.

Table I. Composition of citrate based ethanolamine bath.

Nickel chloride	=	0.1 M
Sodium hypophosphite	=	0.093 M
Sodium citrate	=	0.15 M
Triethanolamine	=	0.15 M
Temperature	=	90°C

Table II. Composition of glycine based ethanolamine baths

Nickel chloride	=	0.1 M
Sodium hypophosphite	=	0.28 M
Glycine	=	0.4 M
Ethanolamine (Mono, di and tri-)	=	0.3 M
Temperature	=	90°C

EN films of about 5 μm thick were deposited on copper foils after thorough cleaning, activated in 0.2 gpl $PdCl_2$ solution and finally rinsing in distilled water.

X-Ray photoelectron spectroscopy

Photoelectron spectra were recorded on a VG Scientific ESCA - 3 MK II electron spectrometer. The samples were analyzed in the as-deposited state, after ion etching in vacuum and after oxidation by exposure to oxygen, air and heating in air. The base pressure in the analyzer chamber of the spectrometer is always less than 10^{-9} torr.

RESULTS AND DISCUSSION

XPS studies on EN deposited from citrate-triethanolamine baths

XP spectra of deposits etched in vacuum showed peaks due to Ni and P only, establishing that deposits were pure. Earlier XPS studies of EN [18,21] showed considerable basic impurities in EN.

Figure 1 shows the XP spectra (Ni 2p region) of etched and oxygen exposed EN deposits. The spectrum A of Fig.1 of the as-plated deposit (after etching) shows the Ni($2p_{3/2}$) peak at 853.2 eV and the Ni ($2p_{1/2}$) peak at 869.9 eV. A small satellite is seen on the higher binding energy side at 5.5 - 6.5 eV from the Ni($2p_{3/2}$) peak. In pure nickel the ($2p_{3/2}$) peak occurs at 852.6 eV [24].

Figure 2 shows the He II UP spectra of pure nickel and that of EN. The valence band of EN shows a shift (with respect to the valence band of nickel) of +0.2 eV and +0.6 eV respectively for 4.3 and 15.5% phosphorus deposits. These shifts may imply that Ni in EN is present as $Ni^{\delta+}$ species.

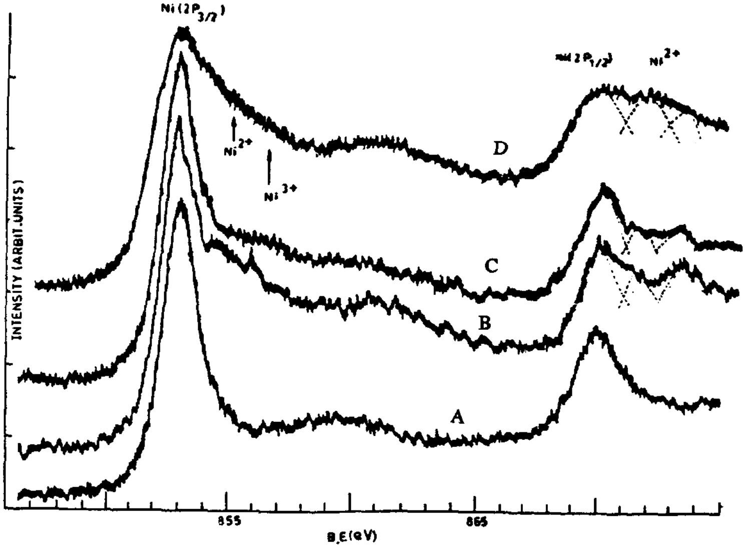

Fig.1.XP spectra of CT-EN (Ni region) A: 4.3% P deposit (etched) B:12.5% P deposit (exposed to oxygen);C:15.5 P deposit (exposed to oxygen); D: 12.5%P deposit heated in air at 400°C(1hour).

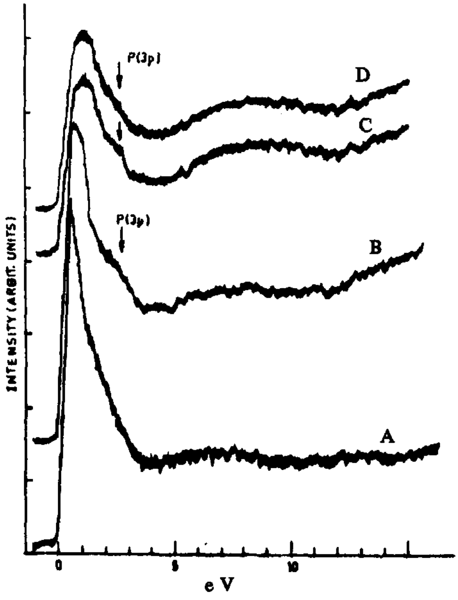

Fig.2.He II UPS of etched nickel and CT-EN
A: Ni; B:4.3%P (EN); C: 15.5% P (EN); D:15.5%P (EN) heated at 400°C for 1 hour.

Figure 3 shows the XP spectra of EN in the phosphorus 2p region. It is seen from the spectrum A that the P(2p) peak occurs at 129.7 eV for CT-EN 15.5% P. Binding energy for P(2p) level in red phosphorus is 130.2 eV [25]. Therefore, the P(2p) peak in EN is shifted by -0.5 eV with respect to the (2p) peak of red phosphorus. P(2p) emission is seen to be shifted to the same extent (-0.5 eV) in the case of oxygen exposed samples (B and C of Fig.3). Further, it is noticed that the shift is 0.5 eV for 4.3% P deposit as well as 15.5% P which indicates that the shift is independent of the concentration of P. The direction of the shift of the 2p emission of P shows that it is in a negatively charged state (P$^{\delta-}$). The occurence of P (3p) emission in He II UPS (Fig.2) at a value lower than the normally expected value of 10 eV lends further support to this inference.

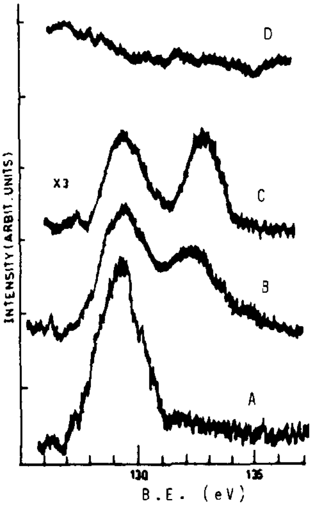

Fig.3 XP spectra of CT-EN deposits - Phosphorus 2p region; A:15.5% P (etched); B:4.3% P (exposed to oxygen); C:15.5% P (exposed to oxygen); D:12,5% P (heated in air at 400°C for 1 hour)

The intensity ratio of the Ni(2p$_{3/2}$) peak to the P (2p) peak is found to be the same for the surface and bulk. Hence, there is no segregation of P or Ni in CT-EN in the as-plated condition. No change in surface concentration of P could be detected even after heating the deposit to 850 K in vacuum.

From spectra B and C in Fig.1 it is seen that additional peaks at 854.9 and 856.5 eV, identifiable respectively as Ni^{2+} and Ni^{3+}, are discernible in the oxygen exposed samples. The $Ni(2p_{1/2})$ region also exhibits three peaks (869.9, 871.8 and 873.5 eV) which are identifiable as due to the presence of $Ni^{\delta+}$, Ni^{2+} and Ni^{3+} species in EN.

Spectrum D in Fig.1 of CT-EN (12.5%P) heated in air at 400°C also shows peaks due to $Ni^{\delta+}$, Ni^{2+} and Ni^{3+} species The presence of a large amount of Ni^{2+} makes the Ni^{3+} peak ill-defined.

Spectra of oxygen exposed samples in the P(2p) region (B and C in Fig.3) show peaks at 129.7 and 132.8 eV. The lower binding energy peak is due to $P^{\delta-}$ species. The higher binding energy peak can be ascribed to be due to P^{5+} species since the P (2p) peak in Na_2HPO_4 occurs at 133.1 eV [26]. The presence of two P species can be deduced from the asymmetry of P (3p) around 9.5 eV in He II UPS of oxygen exposed samples (Fig.4) A similar double peak can also be seen in the spectra reported by Papini and Papini [19] though they did not interpret it in terms of the double peak. Ivanov *et al* [20] also observed P (2p) peaks at 129.7 and 132.5 eV which were ascribed respectively to P^{0} and P^{5+}. They however, did not comment on the negative shift of the P (2p) peak. The absence of P on the surface is deduced from the spectrum of CT-EN (12.5%P) (spectrum D in Fig.3) heated in air (400°C).

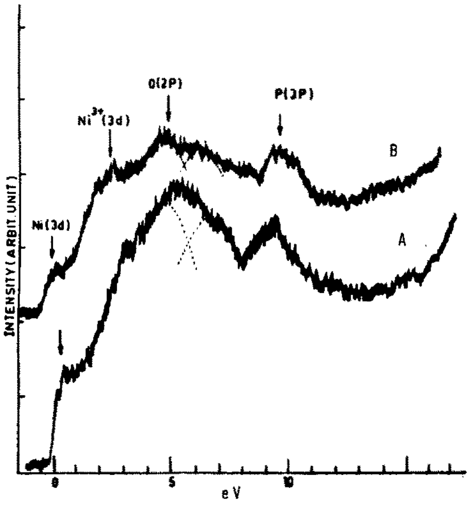

Fig.4. He II UPS of CT-EN exposed to oxygen A:15.5% p; B:4.3% P.

The oxygen 1s region of the XP spectra of CT-EN is shown in Fig. 5. The as-plated sample, after etching, is seen to be free from oxygen (spectrum A of Fig.5). The spectrum (D of Fig.5) of the sample (CT-EN(12.5%)) heated in air at 400°C shows O (1s) emission at 529.9 eV. From spectra D of Figs.5 and 3, it is seen that the surface of this sample does not contain P but only nickel species (Ni^{2+} and Ni^{3+}). Hence the 529.9 eV peak can be ascribed to oxygen associated with nickel as oxide.

Spectra (B and C of Fig.5) of samples exposed to oxygen exhibit a double peak; one at 529.9 eV and another at 531.8 eV. By analogy with the spectrum of a sample heated in air, the lower binding enrgy (529.9 eV) peak can be assigned to oxygen of nickel oxide. The higher binding energy peak is seen whenever P^{5+} species is detected. The two oxygen species are also identifiable from He II UPS of EN (Fig.4) which is consistent with these deductions.

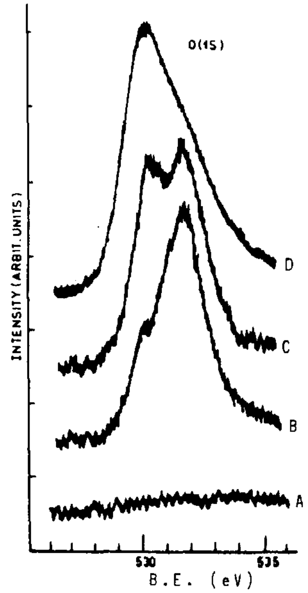

Fig.5 XP spectra of CT-EN deposits - oxygen 1s region; A:4.3% P (etched); B:4.3% P (exposed to oxygen);C:15.5% P (exposed to oxygen); D:12.5% P (heated in air at 400°C)

At this stage one could attempt at the identification of the compounds present on the surface of EN in the as-plated condition. A comparison of the relative intensities of the two O(1s) peaks, shows that the amount of oxygen associated with P is more than that associated with Ni. Taking this fact together with the observation that as-plated and oxygen exposed samples always contain P^{5+}, the most probable species responsible for the higher binding energy O (1s) peak is phosphate. The intensity ratios of the Ni^{3+} emission, P^{5+} and O (1s) at 531.8 eV show that virtually all the Ni^{3+} is present as $NiPO_4$. By considering the other oxide species to be NiO one is able to account for the observed intensities of the Ni^{2+} and the O (1s) emission with a binding energy of 529.9 eV. The as-plated sample probably does not contain any Ni_2O_3. Comparing the relative ratios of intensities of Ni^{2+} and Ni^{3+} and two O (1s) peaks and assuming Ni^{2+} and Ni^{3+} are present respectively as NiO and $NiPO_4$, it is estimated that the amount of surface $NiPO_4$ species present in as-plated CT-EN (4.3% P) and CT-EN (15.5% P) is nearly the same. However, the surface concentration of NiO appears to be greater in 4.3 % P EN deposit than in EN containing 15.5% P.

The satellite (Fig.1) on the higher binding energy side of Ni $2p_{3/2}$ occurs in both the etched and oxygen exposed samples. In the former, it is probably due to charge transfer excitation between Ni and P whereas in the latter case it may be ascribed to **charge transfer excitation between Ni and O.** **A similar satellite** is seen in the XPS of EN reported by others [18,19 and 21].

XPS studies on EN deposited from gylcine ethanolamine baths

XP spectra of GM,GD and GT (M,D and T refer to mon-, di- and tri-ethanolamine) deposits are similar and hence typical results of EN deposited from the GT bath alone are considered. The as-plated deposit shows Ni($2p_{3/2}$) peaks at 853.2 and 856 eV showing that the surface contains both $Ni^{\delta+}$ and Ni^{3+}. The P (2p) emission is seen to consist of two peaks at 129.7 and 132.6 eV (Fig.6). The lower binding energy peak could be ascribed to $P^{\delta-}$ species and the higher binding energy peak to P^{5+} species. It shows a broad unsymmetrical O (1s) emission (Fig.7) which could be resolved into two components with binding energy of 529.8 and 531.9 eV. By analogy with XPS of CT-EN, the higher binding energy O(1s) peak can be ascribed to oxygen associated with P^{5+} as phosphate. The lower binding energy peak of O (1s) can be assigned to oxygen associated with nickel as nickel oxide.

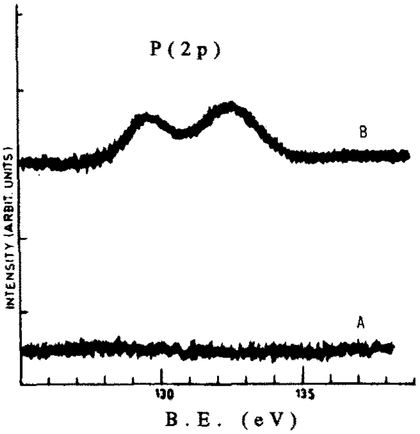

Fig.6. XP spectra of GT-EN (4.8% P) deposit - Phosphorus 2p region A: heated in air at 400°C for 1 hour; B: as deposited condition.

The presence of Ni^{3+}, P^{5+} and O (1s) at a higher binding energy of 531.9 eV indicate that one of the probable surface species is $NiPO_4$. From the relative intensities of O (1s) emissions at 529.8 and 531.9 eV (Fig.7), it is deduced that the surface species in the as-plated condition is predominantly nickel and the oxide content is quite small.

On etching, the O (1s) emission completely disappears. On exposing the etched sample to oxygen an O (1s) emission reappears. The spectra of an oxygen exposed sample and an as-plated sample are similar.

The etched sample exhibits the $Ni(2p_{3/2})$ peak at slightly higher binding energy (852.8 eV) as compared to that of pure nickel (852.6 eV) indicating that nickel is present as $Ni^{\delta+}$. A satellite at 850.1 eV is also seen. This is probably due to charge transfer excitation from the P (3p) to the Ni(3d) orbital. P (2p) is seen at binding energy of 129.7 eV which is slightly lower than the binding energy of red P (130.2 eV) indicating that the species is $P^{\delta-}$.

The intensity ratio of $Ni(2p_{3/2})$ peak and P (2p) peak in the as-plated sample and the etched samples show that $Ni:P:PO_4$ is 24:51:25 in the as-plated deposit and Ni:P is 24:76 in the etched

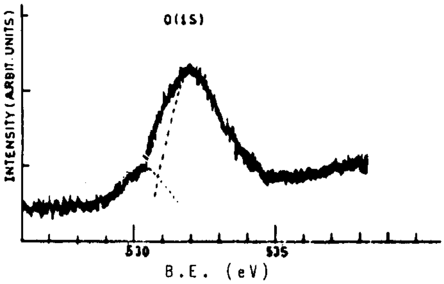

Fig.7 XP spectra of GT-EN (4.8% P) oxygen 1s region

sample. This indicates segregation of P to the surface. Preferential segregation of P to the surface could be due to its low heat of evaporation or due to the strain energy [27]. The heat of evaporation of P is 2.97 Kcal/gm-atom while that of Ni is 91 Kcal/gm-atom. If this difference is responsible for segregation, then one would have noticed it in CT-EN deposits also. Since it is not observed in the case of GT-EN deposits, it is inferred that the segregation in GT-EN deposit might be due to large strain in the deposits. Segregation of P might be the cause for the predominant formation of phosphate on the surface of the as-plated deposit and on that exposed to oxygen.

Comparison of the results of XPS study of CT-EN and GE-EN

Comparing the results of XPS study of EN from CT and GE baths, the following remarks may be made:

1. Both EN deposits contain Ni and P as $Ni^{\delta+}$ and $P^{\delta-}$.
2. CT-EN deposits do not show any segregation of P at the surface whereas EN deposited from glycine baths exhibits surface segregation of P.
3. The surface film of deposit in the as-plated condition is virtually $NiPO_4$ in the case of GE-EN deposits, while it consists of both NiO and $NiPO_4$ in the case of CT-EN.

The nature of phosphorus species in EN

The nature of phosphorus in EN can be discussed in the light of the results presented.

The shifts in the binding energies of 2p levels of nickel and phosphorus show the formation of $Ni^{\delta+}$ and $P^{\delta-}$. This deduction regarding the nature of effective charge on Ni and P agrees with that arrived at by Ching [28] and Chen *et al.* [29] through theoretical calculations. These results contradict the direction of charge transfer proposed by Mott [30] to explain the decrease in the magnetic moment of nickel due to alloying with non-transition elements which was used by Albert [31] to explain the dependence of magnetization of nickel on concentration of phosphorus. The results reported in this paper also do not support the theory of 'rigid band charge transfer model' [32] proposed to explain the magnetic properties of metallic glasses, in which it is assumed that a transfer of one or more electrons **takes place from the metalloid atom to the d band of the transition metal. The applicability of this model has however been questioned already [33].**

The occurrence of emissions at 2.5 eV and 7.5 eV in the valence band spectrum of EN and their absence in the spectrum of pure Ni (Fig.2) indicates an interaction between P (3p) and Ni(3d) orbitals. The energy level diagram given by Szasz *et al* [34] lends support to such an interaction. From a soft X-ray emission spectroscopic (SXES) study of melt quenched Ni-P alloys, Tanaka *et al* [35] concluded that in these alloys, p bands of P hybridize with d bands of nickel which supports our conclusion. Similar hybridization between phosphorus p-states and nickel d-states has been pointed out from a study of the optical properties of melt quenched Ni-P alloy by Rivory *et al* [36].

The valence band spectrum of EN does not show any change when the sample is heated at 400°C (C and D of Fig.2) which is well beyond the crystallization temperature, of EN. It has been shown that at temperatures above crystallisation temperature, EN transforms from amorphous phase into fcc Ni and bcc Ni_3P. In other words, compound formation takes place. If the chemical interaction between Ni and P is brought about only during crystallization, then the spectra of deposits in the as-plated condition and in the heat treated state would be different. The absence of such a difference points out that chemical interaction between Ni and P has already taken place during the deposition of EN. The fact that ΔH for crystallization is much smaller than ΔH of formation of Ni_3P from Ni and P [37] supports this conclusion.

It is reported that the chemical shift of the Ni ($2p_{3/2}$) emission increases with concentration of P while the chemical shift of P (2p) does not vary with the concentration of P. This means that the effective charge on the P atom is independent of phosphorus content of EN but that on the Ni atom depends on the phosphorus content of the deposit. This observation can be understood in terms of the theoretical result of Ching [28]. He has shown that the net charge on the Ni atom depends on the number of nearest neighbor (NN) P atoms. In EN, P-P contact is unlikely, and therefore each P atom will have nearly the same environment in EN with different compositions It is conceivable that Ni atoms will have a much wider distribution of the number of NN **P** atoms, which will depend on the composition of EN. Consequently, the effective charge (hence chemical shift) of Ni will depend on the composition of EN, while the partial charge on P (hence chemical shift) will not depend on the P content of EN. Such a behavior can also be inferred by comparing the theoretical results of Chen *et al.* [29] with those of Ching [28]. Ching [28] calculated the net charge on P in Ni_3P to be -0.5 and felt that a value of -0.3 to -0.4 is more realistic in view of the fact that his calculations had not been carried out to self-consistency. Chen *et al.* [29] calculated the charge on P in Ni_3P to be -0.384. Similarly values obtained for different compositions of Ni-P alloy point out that partial charge on P is independent of composition.

CONCLUSION

In conclusion, it can be stated that the passivity of electroless nickel deposits is due to presence of the charged specis of Ni and P.

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